PATENT SPECIFICATION

1,082,046

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Drilling Mud Additives

We, MILCHEM INCORPORATED, a Corporation incorporated under the Laws of the State of Delaware, United States of America, of 3920, Essex Lane, P.O. Box 22111, Houston, Texas 77027, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Drilling muds generally contain various types of organic polyelectrolytes and other components. Such organic polyelectrolytes are organic oil insoluble hydrophylic materials and they include various lignosulphonates, lignites and polyphenolic compositions. The lignosulphonates used in drilling muds are produced by the reaction of lignin with a sulphonic acid or a sulphite salt. Lignosulphonates are customarily produced by treating lignin contained in wood chips with sodium bisulphite to produce a liquor containing lignosulphonate which is removed from the insoluble residue and purified in various degrees primarily by the removal of sugars. Lignosulphonates known in the oil drilling art are sold under the trademarks "Uni-Cal", "Q-Broxin", "Kembreak" and "Peltex". Lignite as used in drilling muds is the organic mineral which is usually processed only by treatment with sodium hydroxide to render it water soluble. Commercial examples of such lignites are known by the trademarks "Ligco", "Carbonox", and "Tannathin". Suitable polyphenolic compositions are produced from bark and wood from various trees by leaching with hot water to remove tannin and other water soluble compounds. Some manufacturers merely dry the leached material to produce a commercial product, and other manufacturers process or treat the extracts in various ways to produce proprietary products. Commercial examples of the polyphenolic compositions are available under trademarks such as "Rayflo", "Mil-Flo", and "Palcotan". "Mil-Flo" and "Rayflo" have been described by the manufacturer as products derived from hemlock bark and that they comprise modified copolymers of catechin and leucocyanidin with a high content phenolic hydroxyls. "Palcotan" is a causticized tannin product. It is desirable that drilling muds containing organic polyelectrolytes be maintained at an alkaline pH during use, but this gives rise to difficulties since when caustic soda is employed to yield to alkaline pH, reaction of sodium and hydroxyl ion with the formation clays can produce swelling and sloughing of the walls of the bore hole, causing fill-up in the bore hole and creating undesirable operating situations. Further, it is a particularly hazardous chemical which, if not handled carefully can cause severe damage to the skin and eyes.

Further, the buffer capacity of caustic soda is almost non-existent and the addition of caustic induces extreme pH changes in localized areas which accelerate clay reactions causing cleavage and greater surface area which subsequently affects the rheology of the mud system. Moreover, when caustic soda is used, its extreme solubilizing tendency can frequently impair the efficiency of a thinner, both from a dispersant and filtration control point of view. Other alkaline materials, such as lime hydrate, soda ash, and sodium silicates, have found only limited use, and none of these materials in themselves are completely adequate.

This invention relates to drilling mud additives that do not suffer in use from many at least of the disadvantages which arise when caustic soda is used alone but which are buffering agents for drilling muds and which result in improved rheological and filtration properties.

Drilling mud additives according to the invention are formed from compounds which comprise an organic polyelectrolyte, sodium

silicate and an alkali metal hydroxide. They may be formed simply by mixing the three compounds in solution. Thus the additives are formed before being mixed with the drilling mud. We believe that this is necessary to allow some form of reaction to occur, probably between the polyelectrolyte and silicate. The organic polyelectrolyte is preferably present in an amount of from 2 to 30% by weight of the mixture formed from the polyelectrolyte, silicate and alkali, while the silicate is a sodium silicate preferably present in an amount of from 40 to 75% by weight, and the alkali, which is preferably potassium hydroxide, is preferably present in an amount of from 5 to 30% by weight. The additive may be in either dry or liquid form and, when liquid, may be about 50% solids.

The organic polyelectrolyte is an organic oil insoluble hydrophilic material, and may be a lignosulphate, a lignite or a phenolic composition such as a bark extract. The materials of these types already listed as examples of polyelectrolytes which may be contained in the drilling muds are expamples of suitable materials. Of these various organic polyelectrolytes, it has been found particularly desirable to use an organic polyelectrolyte obtained as a bark extract derivative in the form of a sulphonate salt of polyphenolic hydroxyl compounds obtained from Douglas fir, Anabilis fir and Southern pine. One such polyelectrolyte is sold under the trademark "Rayflo" and is described in United States Patent No. 2,999,108. When the drilling mud additive is used as a dried material, the organic polyelectrolyte may desirably be at the lower end of the range, for example 2½%, and, when used as a liquid product, may be at the higher end of the range, for example 30%.

The sodium silicate employed is in a form in which the proportion of sodium oxide to silica is in the broad range of 0.3 to 3 Na_2O: 1 SiO_2, and, preferably in a narrower range of 0.5 to 2 Na_2O: 1 SiO_2. Sodium orthosilicate, that is 2 Na_2O: 1 SiO_2 has been found to be particularly desirable, although other forms within the ranges described above can be satisfactorily employed.

It is preferred that the alkali metal hydroxide is substantially completely, or is at least in part, potassium hydroxide since it has been found that the potassium ion tends to fix to the clay formation and does not cause undesirable clay formation reactions and swelling to the extent that sodium does. It may sometimes, however, be desirable to use a minor proportion of sodium hydroxide with a major proportion of potassium hydroxide for economic reasons and to provide increased alkalinity. The potassium or other hydroxide is employed in the range of 5 to 30% by weight of the composition and an excess over this range is to be avoided as flocculation may be encountered.

The drilling mud additives of the invention are characterized by simple and accurate pH control and absence of adverse reaction with the drilling formation clay. In addition, protection against corrosion is provided through the employment of the sodium silicate.

Some examples of the invention are now given.

EXAMPLE 1

	Wt. %	Pounds Added On A Dry Basis
Sodium Orthosilicate	45%	1125 lb.
"Rayflo"	25%	625 lb.
Potassium Hydroxide	20%	500 lb.
Sodium Hydroxide	10%	250 lb.
		2500 lb. Dry Solids

The sodium orthosilicate (2 Na_2O: 1 SiO_2) may be prepared in a separate tank by adding 974 pounds of sodium metasilicate (1 Na_2O: 1 SiO_2) followed by the addition of 760 pounds caustic soda to produce a sodium orthosilicate solution having a 65% total solids concentration. The sodium metasilicate solution added will add 609 pounds of water which is subtracted from the 2500 pounds of total water to be added.

In a separate container 1141 pounds of water is added followed by 625 pounds of "Rayflo". This "Rayflo" solution contains 35.4% total solids. When the "Rayflo" has completely dissolved the caustic potash is added as 1000 lbs. of a 50% solution, together with the caustic soda as 500 lbs of a 50% solution and the mixture is well blended.

The resultant "Rayflo" containing solution is added to the sodium orthosilicate solution with agitation and the finished product is then put into five gallon cans, which will contain approximately 59 pounds of a 50% finished buffered drilling mud additive solution, i.e., about 11.8 pounds per gallon.

EXAMPLE 2.

Orthosilicate	90%
Potassium Hydroxide	7%
"Rayflo"	3%

In this example, 72% sodium metasilicate (having a solids content of 58%) was heated to 180°F and to this was added 20% crystal caustic having 76% Na_2O. These two materials reacted to give 100% orthosilicate.

A "Rayflo" solution was prepared by putting the "Rayflo" into a potassium hydroxide solution having 60% solids. The weight ratio of potassium hydroxide solution to "Rayflo" was 2:55:1.

The sodium orthosilicate solution was added, immediately after its preparation, to the Rayflo-KOH solution. These two solutions were added together in proportions such that the final composition on a weight basis would be 90% sodium orthosilicate, 7% KOH and 3% Rayflo. After reaction of the sodium orthosilicate and the Rayflo-KOH, the solution was promptly transferred to a drying plate where it was dried for about three minutes at 325°F.

The dried product of this Example as compared to the liquid product of Example 1, although providing some desirable advantages such as ease in handling, was not quite as satisfactory in operation. Thus, flow properties, were not quite as satisfactory and the water loss was more significantly reduced when the product of Example 1 was employed for pH control.

Comparative results are shown in the Table below for results obtained using products of Examples 1 and 2 contrasted with results obtained when using sodium hydroxide and sodium orthosilicate as additives. The alkali additives were employed in a mud composition of 40% illite to which was added 4 grams "Uni-Cal" and a sufficient quantity of the additive constituents to adjust the pH to 9.5. The "Uni-Cal" product is a specially prepared lignosulphonate containing chemically combined chromium as distinct from metallic chromium. Flow properties were measured initially and again after hot rolling before and after adjustment of pH. In the tests in which the results showing satisfactory performance and improved flocculation are reported in the Table below, the quantity of the alkaline constituents required for pH adjustment was as follows:

NaOH = 12.6 cc (1 ml. = 0.25 g) = 3.15 g.
Na Orthosilicate = 6.3 g.
Composition of Example 1 = 12.8 (50%) solution = 6.4 g.
" " Example 2 = 6.44 g.

TABLE

Base Mud: Illite Treatment: 4 g. "Uni-Cal" = pH Control Agent

	NaOH	Orthosilicate	Ex. 1	Ex. 2
Amount	8.0 cc	3.4 g	9 g	3.57 g.
600 Fann Rdg.	32.5	29	28	25
300 Fann Rdg.	21	18	15.5	15
200 Fann Rdg.	17	15	11.5	12
100 Fann Rdg.	12	10	7	8
6 Fann Rdg.	7	4	1	3.5
3 Fann Rdg.	6	4	0.5	3
IG, lb/100 sq ft	1	1	0	0
pH	9.5	9.1	9.8	9.5
pH After Hot -Rolling: Before Stirring	8.0	7.9	8.3	7.9
pH Adjusted with following amount of alkaline constituent 1.2 cc	1.2 vvcc.	.75 g	2.0 g.	.75 g.

TABLE—*Continued*

	NaOH	Orthosilicate	Ex. 1	Ex. 2
Flow Properties after Hot-Rolling and pH Adjustment				
600 Fann Rdg.	21.5	22	20	20
300 Fann Rdg.	12.5	13.5	10	12
200 Fann Rdg.	9.5	10.5	7	9
100 Fann Rdg.	6	6	4	6
6 Fann Rdg.	2	2.5	1	2
3 Fann Rdg.	1.5	2	.5	1.5
IG, lb/100 sq. ft.	0	0	0	0
10G, lb/100 sq ft	18	50	5	37
pH	9.5	9.5	10.2	9.6
Flow Properties after 16 Hours Hot-Rolling.				
600 Fann Rdg.	20	19	22	19
300 Fann Rdg.	11	10.5	10.5	10
200 Fann Rdg.	8	8	7	7
100 Fann Rdg.	5	5	4	4
6 Fann Rdg.	1	1	1	1
3 Fann Rdg.	1	1	1	1
IG, lb/100 sq. ft	0	0	0	0
10G, lb/100 sq ft	6	9	1	5
pH	8.2	8.0	8.7	—
pH Readjusted and Flow Properties Measured Again				
Amount	1.0	.75 g	1.0	.75 g
600 Fann Rdg.	22	22	22	21
300 Fann Rdg.	14	13.5	11	15
200 Fann Rdg.	10	10	8	12
100 Fann Rdg.	7	7	4	8
6 Fann Rdg.	2	2	1	3.5
3 Fann Rdg.	2	2	0.5	3
IG lb/100 sq ft	0	0	0	0
pH	9.6	9.6	10.2	9.8
Flow Properties after Hot-Rolling 11 Hours				
600 Fann Rdg.	19	18	22	20
300 Fann Rdg.	10.5	10	11	10.5
200 Fann Rdg.	8	7.5	8	7.5
100 Fann Rdg.	4.5	4.5	4	4
6 Fann Rdg.	1	1	1	0.5
3 Fann Rdg.	1	1	1	0.5
IG, lb/100 sq ft	0	0	0	0
10G, lb/100 sq ft	8	8	1	6
pH	8.6	8.5	9.3	8.7
Flow Properties after pH Adjustment				
Amount	0.7 cc.	.5 g.	0.2 g.	.5 g.
600 Fann Rdg.	21	22	20	28
300 Fann Rdg.	13	13	10	17
200 Fann Rdg.	10	10	7	13
100 Fann Rdg.	6	7	4	9
6 Fann Rdg.	2	2	1	4
3 Fann Rdg.	2	2	1	4
IG, lb/100 sq ft	0	0	0	1
pH	9.6	9.5	9.5	9.9

TABLE—*Continued*

	NaOH	Orthosilicate	Ex. 1.	Ex. 2.
Properties after Hot-Rolling				
600 Fann Rdg.	21	19	22	20
300 Fann Rdg.	12	10	11	11
200 Fann Rdg.	8	8	7	8
100 Fann Rdg.	5	5	4	5
6 Fann Rdg.	1	1	1	1
3 Fann Rdg.	1	1	1	1
IG, lb/100 sq ft	0	0	0	0
10G, lb/100 sq ft	8	8	1	7
pH	8.4	8.6	9.0	8.8
Flow Properties after pH Adjustemnt				
Amount	.7 cc	.5 g	.25 g	.5 g
600 Fann Rdg.	21	30	20	30
300 Fann Rdg.	12	19	10	20
200 Fann Rdg.	9	15	7	16
100 Fann Rdg.	5.5	11	4	12
6 Fann Rdg.	1.5	5	1	7
3 Fann Rdg.	1	5	1	7
IG, lb/100 sq ft	0	1	0	3
pH	9.6	9.6	9.8	10.1
Flow Properties after Hot-Rolling				
600 Fann Rdg.	22.5	22	22.5	23
300 Fann Rdg.	12	11.5	11.5	12
200 Fann Rdg.	9	8.5	8	9
100 Fann Rdg.	5	5	4	5
6 Fann Rdg.	1	1	0.5	1
3 Fann Rdg.	1	1	0.5	1
IG, lb/100 sq. ft	0	0	0	0
10G, lb/100 sq ft	8	9	1	9
pH	8.8	9.2	9.1	9.3
Flow Properties after pH Adjustment.				
Amount	0.5 cc	0.2 g	0.2 g	0.2 g
600 Fann Rdg.	22	24	19.5	27.5
300 Fann Rdg.	13	13.5	10	16
200 Fann Rdg.	9.5	10.5	7	11.5
100 Fann Rdg.	6	6.5	3.5	7
6 Fann Rdg.	1.5	1.5	0	2
3 Fann Rdg.	1	1	0	2
1G, lb/100 sq ft	0	0	0	0
pH	9.6	9.7	9.5	9.9

	NaOH	Orthosilicate	Ex. 1.	Ex. 2.
Flow Properties after 16 Hours Hot-Rolling				
600 Fann Rdg.	21	21	22	24
300 Fann Rdg.	12	11.5	11	13
200 Fann Rdg.	9	8	7.5	9.5
100 Fann Rdg.	5.5	5	4	5.5
6 Fann Rdg.	1	1	0	1.5
3 Fann Rdg.	1	0.5	0	1.5
IG, lb/100 sq ft.	0	0	0	0
10G, lb/100 sq ft.	9	9	0.5	9
pH	8.8	9.1	9.2	9.2
API Filtrate, ml	13.7	12.0	10.4	12.8
pH Readjusted to	9.6	9.7	9.7	10.0
Amount	0.5 cc	0.2 g	0.2 g	.17 g
Flow Properties after NMuds Aged at 300°F.				
700 Fann Rdg.	32	28	20	25
300 Fann Rdg.	22	17.5	10.5	15
200 Fann Rdg.	18	14	7.5	12
100 Fann Rdg.	14	10	4	8
6 Fann Rdg.	12.5	5	0.4	3
3 Fann Rdg.	11.5	4	0.5	3
IG, lb/100 sq ft.	6	0	0	0
10G, lb/100 sq ft.	49	31	5	27
pH	7.3	7.5	7.5	7.6
ApI Filtrate, ml	13.5	11.4	11.0	12.0

In the Table 'Fann Rdg.' is an abbrevation for a reading taken on a Fann viscometer, the prefix number referring to the speed of rotation in r.p.m. of the rotating sleeve of the instrument; 'I.G.' is an abbreviation for Initial Gel and is a measure of gel strength of a drilling fluid immediately after agitation has ceased; '10 G' represents the gel strength 10 minutes after agitation has ceased and the term 'Hot-Rolling' refers to a process in which drilling conditions are simulated by working a drilling fluid in a heated chamber equipped with rotating rollers.

The buffered drilling mud additives of the invention meet the requirements of additives that are capable of furnishing the required alkalinity and eliminating, or at least reducing very significantly to a workable level, the above caustic soda disadvantages and have made possible the substantially complete activation and control of the rheology and pH of organic polyelectrolyte muds.

The sodium silicates employed in this invention are alkaline in solution, and the pH of the various silicate solutions is proportional to the Na_2O present. Electrometric titrations with acid has demonstrated that the high pH of silicate solutions are maintained until the alkali is almost completely neutralized and that this buffer capacity increases with increasing proportions of soluble silica.

Initial investigations demonstrated the ability of sodium orthosilicate and sodium metasilicate to activate organic polyelectrolyte clay suspensions and subsequently induce a reduction in flow properties, which in non-contaminated tests, were more significant than that obtained from a comparable caustic soda treatment. It was noted that the muds containing the silicate materials had higher API filtrates than the causti-soda-treated muds. Accordingly, it was necessary to develop a pH control agent capable of furnishing filtration control as well as rheological properties superior to that afforded by either caustic soda or sodium silicates. The present invention of a drilling mud additive formed from an organic polyelectrolyte and sodium silicate, together with an alkali metal hydroxide, preferably potassium hydroxide, has provided a synergistic effect in the alleviation of the water loss problem as well as providing improved viscometric properties which were especially significant after aging the muds at 300°F. and higher temperatures. Further, the problem of promoting clay base reactions has been substantially solved. The rheological properties and filtration control are far superior to that afforded by caustic soda. The buffered drilling mud additives of this invention induces reduction in viscosity in various organic polyelectrolyte treated system, such as the "Uni-

Cal", mentioned above, as well as "Q—Broxin", which are both lignosulphonates, and, in addition, works advantageously on lignite treated muds to provide results that are much more significant than that obtained from the addition of caustic soda. The buffered drilling mud additive has been further tested as a dispersant and proves to be quite effective in both sodium bentonite and native solid muds.

To illustrate the comparative alkalinity and buffering and neutralization properties of the buffered drilling mud additive of this invention as compared to caustic soda, reference is made to Figure 1 and 2 of the accompanying drawings. Figure 1 shows the comparable pH values of the buffered drilling mud additive and caustic soda as their concentration varies. Figure 2 shows the buffer capacity of the buffered drilling mud additive as compared to caustic soda. As shown in Figure 2, it is most difficult to "creep-up" on the pH of the solution or suspensions treated with caustic soda, and, invariably, should a pH of 9.5 be desired as an example, and is quite often the case in drilling mud systems, this pH cannot be easily obtained. This is to be contrasted with the buffered drilling mud additive curve where a workable range is provided so that the pH can be easily obtained without fear of overshooting the desired pH.

Figure 3 of the accompanying drawings shows the comparative viscosity of a typical "Uni-Cal" mud at various pH's where the pH is controlled on the one hand by sodium hydroxide and on the other hand by the buffered drilling mud additive of the invention. The curves show that the viscosity of the mud system is substantially reduced at a lower pH for the buffered drilling mud additive as compared to the use of caustic soda. Figure 4 of the accompanying drawings shows the comparative viscosity of a mud with the buffered drilling mud additive and caustic soda after hot rolling and after varying periods of time, and demonstrates the difference between the effect of NaOH and synergistic on clay slurries of 27.4 Illite suspended solids over extended time. The increase in viscosity of the clay slurry treated with NaOH is due to hydroxyl clay cleavage which results in an increase in surface area of the clay particles.

A typical application of the buffer drilling mud additive of this invention will be described in drilling the Anahuac and Frio shales along the Texas Gulf Coast. These shales have been quite troublesome and have affected both drilling operations and mud control. While drilling these shales, penetration rates have usually been controlled to prevent bit balling and sloughing. In addition, a slower drilling rate has often been necessary to clean out the hole and to catch up on the mud treatment. Such practices have invariably increased overall drilling costs because more drilling days have been required to reach total depth. The buffered drilling mud additive of this invention, such as the product of Example 1, has been employed to obtain optimum performance in drilling these shales, in meeting the capabilities of handling the greatest possible drilling rates and in eliminating time consuming operations such as reaming tight spots, circulating bottoms-up, short trips, or conditioning mud. The mud has exhibited minimum yield points to utilize the maximum available hydraulic horsepower for optimum penetration rates. Further, the mud has been easy to control and maintain with chemical treatment costs kept at a reasonable limit.

A typical example of use for the product of Example 1 has been that for a Brazoria County drilling operation in Texas. After setting 2000 feet of 10¾ inch surface casing, a 9⅞ inch hole was drilled to 6800 feet. At 6800 feet, the mud system was converted to a "Uni-Cal" oil emulsion mud employing 5 pounds per barrel of "Uni-Cal" and 1½ pounds per barrel of the drilling mud additive of Example 1, and 10% by volume diesel oil. At this time the mud had the following properties:

Mud Weight, ppg	9.1
Funnel Viscosity, sec.	43
Apparent Viscosity, cp	17
Plastic Viscosity, cp	12
Yield Point, lb/100 sq. ft.	8
Gels, lb/100 sq. ft.	0/8
API Filtrate, mol	4.9
% Oil by Volume	9.5
% Solids by Volume	10
pH	8.1
Chlorides, ppm	1800
Calcium, ppm	70

The above properties were obtained at a time when rapid drilling rates make it most difficult to condition the mud. These properties, although not considered ideal from a plastic viscosity to yield point ratio relationship, were all that were required for maximum penetration rates. With the mud doing all that was required, the operating personnel saw no need to spend additional money to condition the mud to improve the plastic viscosity to yield point ratio. This particular mud served to drill more than 1700 feet of hole in two days after the initial mud conversion. With such penetration rates it becomes a matter of necessity not to attempt to establish high plastic viscosity to yield point ratios. This is simply a practical situation where less than ideal mud characteristics provide satisfactory and safe fast hole drilling at a desired cost.

At greater depths into the Frio shale, the pH of the mud was gradually raised to 9.0 with the buffered drilling mud additive. An improvement in the flow properties of the mud was noted when the pH was raised. The pH was then maintained between 9.0 and 9.2 for the remainder of the drilling operation. On the fifth day after conversion at 9780 feet, the mud exhibited the following properties:

Mud Weight ,ppg	11.0
Funnel Viscosity, sec.	48
Apparent Viscosity, cp	29
Plastic Viscosity, cp	27
Yield Point, lb/100 sq. ft	4
Gels, lb/100 sq ft	0/0
API Filtrate, ml	3.8
%Oil by Volume	9.0
% Solids by Volume	17.5
pH	9.0
Chlorides, ppm	2300
Calcium, ppm	100

Recommended hourly treatments at this time included 10 bags of "Uni-Cal" and 5 cans of the buffered drilling mud additive. Observations of the Anahuac shale coming over the shaker showed a distinct difference from that observed on previous walls in this area. The extreme gumbo-like conditions of the cuttings normally observed with the Anahuac shale was conspicuously absent. In contrast, the shale particles were true bit cuttings with distinct angular edges. In addition, the amount of cuttings appeared to approximate the actual volume of hole drilled showing the absence of swelling. Drilling to target depth was then accomplished without difficulty. During trips for new bits, no abnormal drag was encountered either going in or coming out of the hole.

There was no evidence of fill-up when running the bit to bottom. At no time was the penetration rate held back because of poor hole conditions or time required to condition mud. The excellent drilling performance of this mud made it possible to drill to a total depth of 10805 feet through the Anahuac in 13 days. In contrast to the performance of this mud, a recently drilled offset well required 20 days to reach a total depth of 10620 feet. The reduction of 7 to 8 days rig time with the mud employing the buffered drilling mud additive resulted in a substantial savings to the operator with the achievement of high performance characteristics.

WHAT WE CLAIM IS:—

1. A drilling mud additive formed from compounds which comprise an organic polyelectrolyte, sodium silicate and an alkali metal hydroxide.

2. An additive according to claim 1 in which the ratio $Na_2O:SiO_2$ for the sodium silicate is from 0.3:1 to 3:1, and in which the alkali metal hydroxide is at least in part potassium hydroxide.

3. An additive according to claim 1 or claim 2 formed from a mixture comprising 2 to 30% by weight of an organic polyelectrolyte, 5 to 30% by weight of an organic polyelectrolyte, 5 to 30% alkali metal hydroxide and 40% to 75% of sodium silicate.

4. An additive according to any preceding claim in which a major proportion of the alkali metal hydroxide is potassium hydroxide.

5. An additive according to any preceding claim in whic hthe alkali metal hydroxide is substantially completely potassium hydroxide.

6. An additive according to any preceding claim in which the ratio $Na_2O:SiO_2$ for the sodium silicate is from 0.5:1 to 2:1.

7. An additive according to any preceding claim in which the ratio $Na_2O:SiO_2$ for the sodium silicate is 2:1.

8. An additive according to any preceding claim in which the organic polyelectrolyte is a lignosulphonate, a lignite or a polyphenolic compound derived from bark extract.

9. An additive according to any preceding claim in which the organic polyelectrolyte is a water soluble alkaline bark extract derivative.

10. An additive according to claim 9 in which the bark extract derivative is a sulphon-

ate of hydroxy aromatic polymeric compounds obtained from Douglass fir, Amabilis fir or Southern pine.

11. An additive according to claim 1 substantially as herein described with reference to the Examples.

12. A method of preparing of drilling mud additive according to any preceding claim comprising mixing in solution compounds comprising an organic polyelectrolyte, sodium silicate and an alkali metal hydroxide.

13. A method according to claim 12 comprising mixing a solution comprising sodium silicate with a solution formed from compounds comprising an organic polyelectrolyte and an alkali metal hydroxide.

14. A method according to claim 13 wherein the solvent is evaporated from the resultant mixed solution.

15. A method according to claim 12 substantially as described herein with reference to the Examples.

16. A drilling mud additive prepared by the method of any of claims 12 to 15.

17. An improved drilling mud comprising an additive according to any of claims 1 to 11 and 16.

18. An improved drilling mud according to claim 17 in which the mud without the additive contains a lignosulphonate and combined chromium.

19. An improved drilling mud according to claim 17 substantially as herein described.

20. A method of preparing on improved drilling mud according to claim 17 or claim 18 comprising mixing an additive according to any of claims 1 to 11 or 16 with a drilling mud.

21. A method of drilling in which a drilling mud according to any of claims 17 to 19 is used.

22. A method of drilling according to claim 21 substantially as herein described.

For the Applicants:—
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
51/52 Chancery Lane, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press —1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

FIG.1

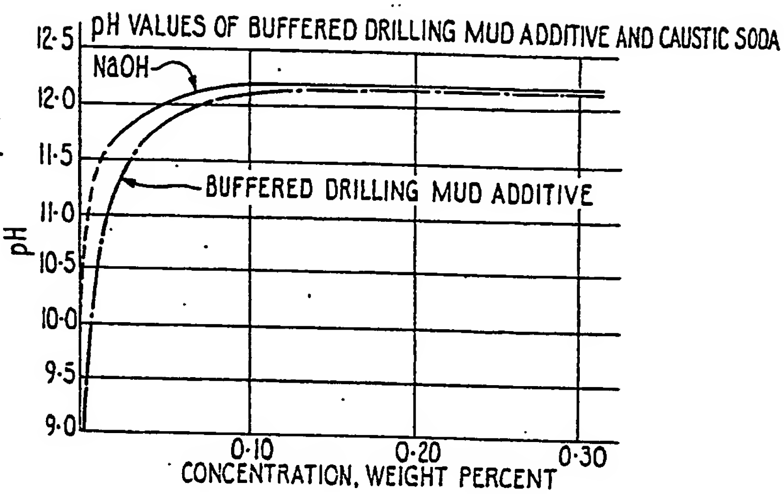


FIG.2

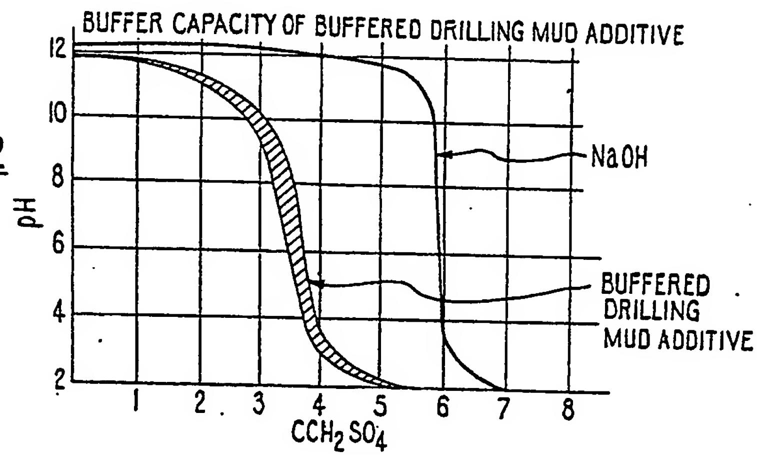
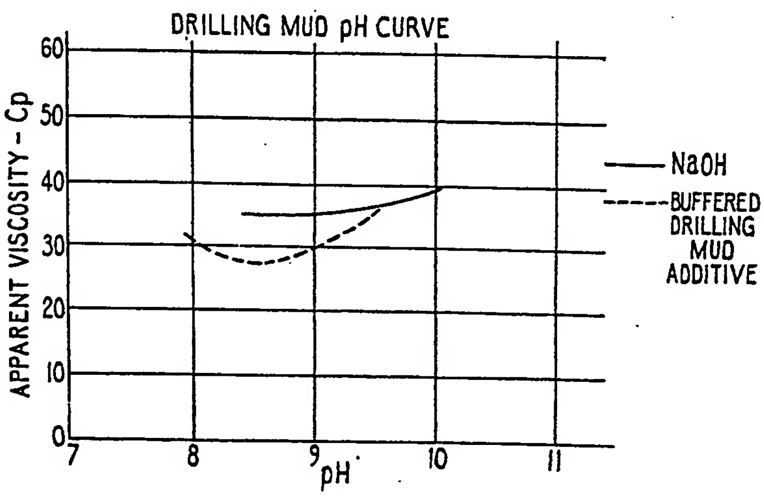


FIG.3



1082046 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheets 1 & 2

I CAUSTIC SODA

'IVE

FERED
LLING
) ADDITIVE

— NaOH
---BUFFERED DRILLING MUD ADDITIVE

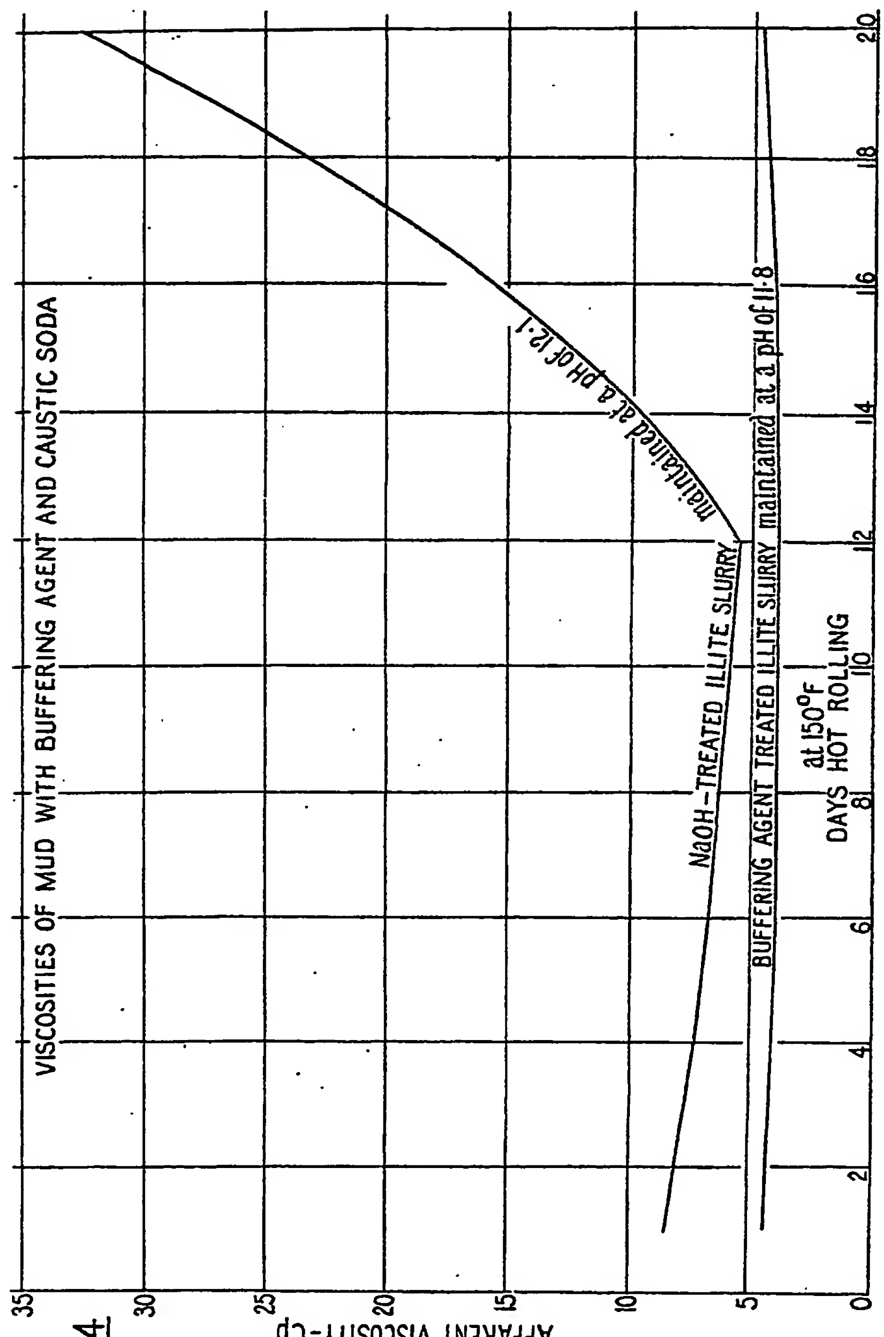


FIG.4

1082046 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheets 1 & 2

FIG.1

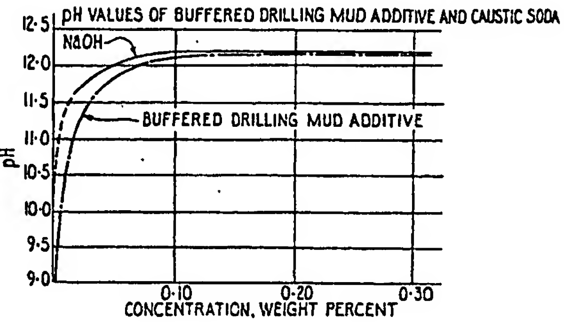


FIG.2

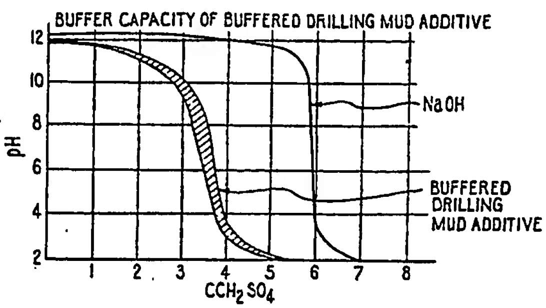
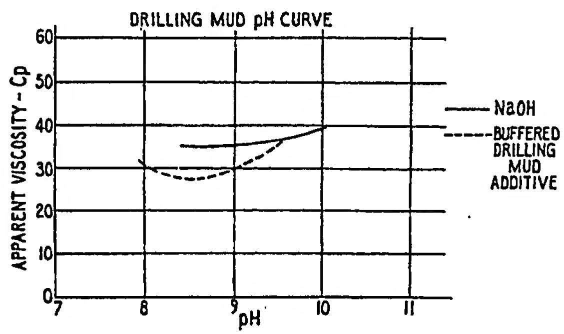


FIG.3



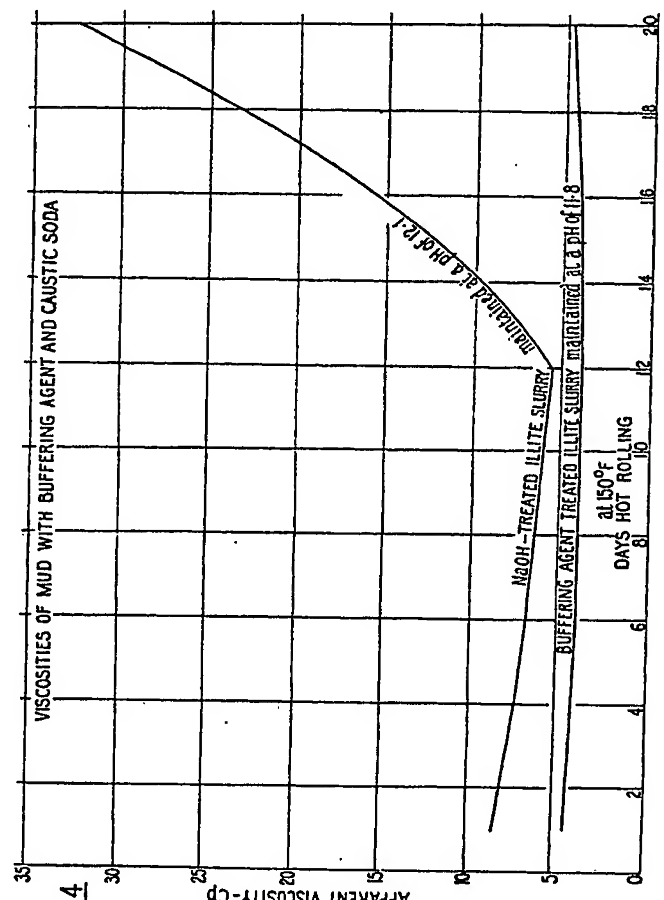


FIG.4

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